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Electrical properties of patterned photoactive layers in organic photovoltaic modules

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ABSTRACT

The scaling of thin film photovoltaics to a commercially viable size relies on the series connection of multiple small cells into modules. These interconnections are typically formed by three patterning steps, each of which have an impact on the series resistance and consequently on the total module performance. Here, we implement the transmission line method for the complete analysis of the P2 patterning step of the photoactive layer in organic photovoltaic modules. Devices are investigated with a sample design that allows for a comparative study of the P2 connection on the solar cell performance. We compare subtractive mechanical scribing to a newly developed additive pre-patterning method for the P2 step. Aerosol Jet printed pre-patterning lines of low surface energy and conductive poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) modified with a fluorosurfactant repel the subsequently spray coated photoactive layer. Furthermore, the influence of MoO_3 in the P2 pattern is elucidated, displaying a substantial increase in series resistance and decrease in device performance.

1. Introduction

Substantial improvements in materials, device architecture, and fabrication techniques over the past decades have brought lab-scale organic polymer photovoltaic device efficiencies to above 10% [1–4]. Industrial coating techniques, such as spray coating, blade coating, and slot die, are being investigated for use in fabricating large area and commercially-relevant devices [5–13]. However, merely increasing the area of single cells is insufficient for up-scaling.

Module performance has been progressing over the years, yet, a large discrepancy exists between large area device and lab-scale device performance [14–16]. This difference is primarily due to resistive losses. To minimize resistive losses in these large area devices, a grid may be included to increase the conductivity of the transparent electrode. However, this method reduces light transmission to the photoactive layer when illuminated though a grid-assisted electrode. A second method to minimize resistive loss is to monolithically pattern the large area into series connected devices [17,18]. In a series connected module, the voltage increases linearly with the number of cells, while the current running through the whole module is identical to that passing through each single cell. An archetypal structuring of a module involves three patterning steps for the deposited layers: P1 separates the bottom electrode between individual cells, P2 removes the active layer to allow contact between the anode and cathode of adjacent cells, and P3 separates the top electrodes of adjacent cells (Fig. 1) [19].

Several factors impact performance when moving to a series connected module structure. The interconnections between individual cells must be narrow to reduce inactive areas, i.e. increase the geometrical fill factor [14,20]. When reporting aperture area efficiency, i.e. the power conversion efficiency of a device calculated using the total device area including the patterned areas, this loss mechanism is apparent in the loss of area that can absorb and produce photocurrent. To analyze the device performance rather than the whole module performance, the area lost to the patterning steps is disregarded and the efficiency is the active area power conversion efficiency. A decreasing shunt resistance can be electrically observed and can be related to non-uniformities in the large active area and to the P1 and P3 steps. Series resistance results from bus bar resistance, owing to the larger distances that the photocurrent must pass through, contact resistance between the layers and contacts, internal photoactive layer resistances, and from issues introduced by the patterning steps. To decrease these

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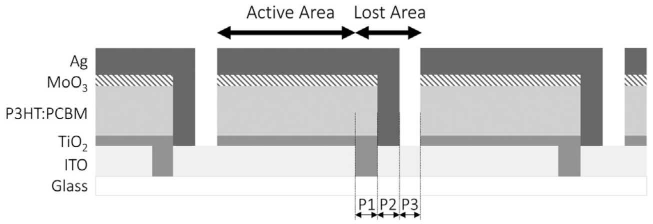

Fig. 1. Schematic representation of the archetypal organic photovoltaic module. Three patterning steps are involved: P1 separates the bottom electrode between individual cells, P2 removes the active layer to allow contact between the anode and cathode of adjacent cells, and P3 separates the top electrodes of adjacent cells.

losses, while up-scaling thin film photovoltaics, the impact of each patterning step must be known and minimized. The impact of the contact resistance at the interconnection of two layers can be determined by the transmission line method (TLM) [21–23]. In a series connected module, the contact resistance is added to the total resistance for every cell in the module, and thus must be reduced to negligible levels to maintain high performance. Different patterning techniques can be objectively compared by the specific contact resistance of each interface.

Patterning may be achieved via subtractive methods, where deposited material is removed, or via additive methods, where the pattern is inherent to the deposition. Subtractive techniques typically combine large area coating techniques with mechanical or laser scribing, [19,24] or with shadow mask application [25,26]. Additive techniques rely on patternable deposition techniques, such as slot die coating, [6] laser printing, [27] ink-jet, [28], flexographic, [29] and gravure printing [30]. Pre-patterning a module substrate with material that is repulsive (low surface energy) to the photoactive material solution enables additive patterning via large-area coating techniques, as an alternative to P2 scribing. Pre-patterning has been demonstrated with ink-jet printed self-assembled monolayers in combination with ultrasonic spray coating [31].

Pre-patterning can be achieved with Aerosol Jet printing, a scalable direct-write deposition technique that can pattern lines down to 10 μm in width. Aerosol Jet printing has been implemented for the fabrication of organic light emitting diodes, [32] metallization of solar cells, [33] transistors, [34,35] and OPV materials [36,37]. The system works by aerodynamically focusing a dense and low velocity aerosol with a set of converging nozzles [38]. The nozzle-to-substrate distance is typically on the order of 5 mm, reducing the implications of near contact with the substrate. Another advantage of the deposition technique is the possibility to deposit inks with a wide range of parameters.

In this work, we investigate the influence of patterning the photoactive layer (P2) on the performance of organic photovoltaic modules. This analysis utilizes both electrical characterization of the device performance and TLM. We compare subtractive scribing and additive pre-patterning techniques on OPV module performance. The pre-patterning technique is developed and optimized in this study. Aerosol Jet deposition is implemented to deposit conductive poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) lines with a fluorosurfactant additive (Zonyl FS-100), as the repulsive pre-patterning line. For pre-patterned devices, ultrasonic spray coating is used to coat the poly(3-hexylthiophene) (P3HT):(6,6)-phenyl C61-butyric acid methyl ester) (PCBM) photoactive layer. Mechanical scribing is employed for the subtractive patterning technique, using a blade to remove material with high precision. Furthermore, the substantial impact of the inclusion of a MoO_3 hole transport layer within the P2 scribe is elucidated.

2. Experimental details

2.1. Materials

The indium tin oxide (ITO) coated glass was purchased from Colorado Concepts ($R_{\text{sheet}} = 16–19\ \Omega\ \square^{-1}$). All solvents were purchased from Sigma-Aldrich. The Clevios P VP Al 4083 PEDOT:PSS dispersion was purchased from Heraeus Clevios GmbH. The FS-100 fluorosurfactant was purchased from Du Pont through Sigma-Aldrich. The regio-regular P3HT was purchased from Rieke Metals, Inc. as #4002-EE. The PCBM was purchased from Nano-C.

2.2. Device fabrication

2.2.1. Substrate, bottom transport layer, and P1

The substrates were patterned using standard photo-lithography, and diced to $5.5 \times 5.5\ \text{cm}^2$ with eight 5 mm wide ITO stripes of 4 cm length. All substrates were cleaned before use in an ultrasonic bath in a sequential application of detergent, deionized water, acetone, and 2-propanol. Titania sol–gel in ethanol was spin coated at 1000 RPM in air to make 5 nm thick layers [17]. The TiO_2 layer acts as the electron transporting layer to form the ITO side cathode.

2.2.2. Subtractive, mechanically patterned devices, P2

The photoactive layer of P3HT:PC_{61}BM (50 wt% PCBM) with a total concentration of 40 g L^{-1} in ortho-dichlorobenzene (ODCB) was spin coated. The substrate was then annealed at 130 °C for 10 min. The P2 mechanical scribing was done with a computer controlled XYZ stage by scraping a thin metal blade over the surface with a constant normal force. A lateral positioning precision of 10 μm was attained [8].

2.2.3. Additive, pre-patterned devices, P2

An Optomec Aerosol Jet 300 was used to deposit low surface energy lines in ambient conditions. The lines were an aqueous blend of PEDOT:PSS and 17 g L^{-1} of fluorosurfactant (Zonyl FS-100). Following the deposition of the pre-patterning lines, the P3HT:PC_{61}BM (50 wt% PCBM) with a total concentration of 9 g L^{-1} in a 70:30 vol% blend of *ortho*-dichlorobenzene (ODCB):mesitylene was spray coated from a Sono-Tek AccuMist 120 kHz ultrasonic nozzle fixed to an ExactaCoat system. The substrate was then annealed at 130 °C for 10 min.

2.2.4. Top transport layer, electrode, and P3

The top transport layer of 10 nm of molybdenum oxide (MoO_3) and 100 nm thick silver electrode were thermally evaporated in high vacuum (10^{-5} Pa). The MoO_3 layer acts as the hole transporting layer, and forms the anodic contact to the photoactive layer. The Ag is used as reflective contact to transport charges from the active area to the ITO of the subsequent cell in a module. The P3 patterning of the top contact was accomplished by mechanical scribing, similar to the subtractive P2 step.

2.3. Characterization

2.3.1. Transmission line method

Unpatterned ITO coated substrates were used for TLM measurements. The P2 lines were patterned in the photoactive layer with center-to-center distances of 3, 4, 6, and 8 mm (10 different measurement lengths) and contact pads were subsequently deposited over the patterns. The total resistance was calculated from the slope of measured current vs. voltage curves between each contact.